PYROLYSIS-FOURIER TRANSFORM INFRARED SPECTROMETRY AS A TECHNIQUE FOR ANALYZING FUNCTIONAL GROUPS WITH OXYGEN IN COAL

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INTRODUCTION

Pyrolysis, flash pyrolysis and thermogravimetric analysis (TGA) were used to characterize coals based on thermolysis products [1-7]. The coals are known to release volatiles such as CO_2 and methane even at sample storage and handling conditions used for Premium Coal samples at Argonne National Laboratory[9,10]. Coal conversion process produces these volatiles in larger quantities. The maximum amount of small species including CO_2 and CO are produced under pyrolytic and gasification conditions. There are reports on the temperature dependance of the thermolysis of functional groups in coal[2,4,5]. The volatiles were quite often identified by using techniques such as GC, MS, GC-MS and FT-IR. Long hydrocarbon chains in Texas lignites and other coals were analyzed by Pyrolysis -GC[1]. Flash pyrolysis using GC-MS was used for determining organic sulfur structures in coal[3]. The use of TGA-FT-IR for coal analysis based on devolatilization products has been reported[6].

Quantification of oxygen in coal is often accomplished by indirect methods. Since the estimation of organic oxygen is interfered by the moisture content and the oxygen in the mineral matter, oxygen content of coal is reported in more than one format[9]. Pyrolysis can convert organic oxygen to oxides of carbon which can be estimated using a gas chronographic detector. A gas chromatograph with detector for organic oxygen is now available from Carlo Erba for estimating oxygenated organic species. The GC effluents are pyrolyzed at 1400°C . The oxides of carbon are converted to methane with hydrogen in the presence of a Ni catalyst, and the methane is then estimated by flame ionization detector. This technique however cannot distinguish CO_2, CO or CH_4, but the concept that pyrolysis converts organic oxygen to oxides of carbon is established.

Using a continuous-mode pyrolyzing inlet for GC, available commercially[8], we have conducted experiments to develop a new technique for analyzing coal, particularly the organic oxygen. The samples are pyrolyzed in a pyrolyzer which is fitted to the injection port of capillary gas chromatograph on-line with FT-IR spectrometer with GC-FT-IR interface. The system allows both qualitative and quantitative analyses. The IR peaks of volatiles are at least a hundred fold larger than what is observed by TGA-FT-IR experiments[6]. Small species such as CO, H_2O and CH_4 often missed by GC-MS are easily identified and even estimated by GC-FT-IR. The results of our preliminary experiments using pyrolysis-GC-FT-IR indicate that useful data on organic oxygen as well as its distribution in various functional groups can be obtained.

EXPERIMENTAL

The pyrolysis experiments were conducted using a number of simple organic compounds which were obtained from commercial sources and contained one or more functional groups with oxygen. Eight Premium Coal samples from Argonne National Laboratory were the coal samples. Table 1 lists some of the reported analysis data of the Premium coal samples[9]. The Texas lignite sample was obtained from a local mine at Carlos about twenty miles away from the campus and was analyzed in the Chemistry Department.

The Instrumental setup consisted of a Pyrojector[8] (Scientific Glass Engineering, SGE, Austin Texas), Fourier Transform infra red (FT-IR) spectrometer (Nicolet 60SXR) with gas chromatographic interface and a capillary gas chromatograph (Hewlett Packard , HP5890) with on-column injection port. The Pyrojector was installed on the on-column injection port using an adaptor made in the machine shop of the Chemical Engineering Department .

Septum injection technique was used. Helium was used as the carrier gas.There were purges at the septum of the pyrojector as well as at the on-column injector. The carrier gas flow through the capillary column was derived from the gas flow through the Pyrojector as well as the carrier gas flow of the gas chromatograph through the injection port. The sample size as well as these flow rates were optimized for quantitative results. The furnace temperature of the pyrojector was varied from 300°C to 1000°C. The GC oven temperature of the gas chromatorgraph was maintained at 50°C. The FT-IR was used as the detection technique. The gas chromatograph was equipped with a 25 meter 0.32 mm id capillary column with 1 um BP-5 (5%phenyl 95% methyl silicon bonded phase, SGE). In this study only smaller species which were volatile in oven at 50°C were detected by FT-IR. A mercury cadmium telluride (MCT-A, Nicolet) detector was used on the gas chromatographic port of the system. The IR spectra were scanned at 4 cm^{-1} resolution. Either 8 or 32 scans were collected per file. The data collection was initiated 1.5 minutes after sample injection and discontinued after 6 minutes. The spectra were collected in this time frame in several files. The spectrum collected just before the appearance of the products was used as background which was subtracted from each sample spectrum.

The instrument was calibrated by injecting 0.25 ml standard gas mixture (2% methane, 20% carbon monoxide, 50% carbon dioxide and 28% nitrogen) using a pressure tight gas syringe. Areas under major IR peaks were used for response factor calculations. Liquid samples were injected using a 10 ul syringe. The initial Prolysis experiments were conducted on acetic acid , ethylacetate, tetrahydrofuran, hydroxybenzoic acid and several other compounds. These compounds represent organic molecules having functional groups with oxygen. Samples were pyrolyzed at temperatures ranging from 400°C to 1000°C in order to determine the optimum temperature for removal of oxygen from these molecules as oxides of carbon. The solid samples were introduced into the Pyrojector either as a pellet (which was prepared using a pelletizer from SGE) or as pressed powder using a solid injector. The sample sizes were 1 mg for pure organic compounds. About 2 mg samples were used for coals. The sample size was not very precise as the powder was packed into the barrel of the solid injector (mostly same volume of powder) and pushed into the inlet of the Pyrojector.

Experiments were also conducted using cryofocussing technique. During the first five minutes after sample injection the volatiles were trapped by cooling a small segment of the capillary column in liquid nitrogen. After five minutes the column was removed from liquid nitrogen and allowed to warm up while scanning the IR spectrum.

RESULTS AND DISCUSSIONS

Making the pyrolysis experiments reproducible was very challenging. Several initial experiments were irreproducible due to leaks and noncompatible flow conditions. The pyrojector was composed of quartz pyrolyzing tube which was heated in a furnace with free standing control module. The samples were injected from the top of the tube through the septum and the pyrolyzed products were immediately swept into the capillary column and to the light pipe of the GC-FT-IR interface. The carrier gas He entered from the top of the pyrojector as well as through the inlet of GC. The gas head pressures at these points were optimized for better detection. This was achieved by varying the head pressures while injecting acetic acid samples. 10 psi He pressure at the Pyrojector head was found suitable while the pressure at the column inlet was kept slightly lower. Both the septum purge of the Pyrojector and GC inlet purge were kept at a level of less than 1 ml per minute. Higher purge flows caused the escape of products.The experiments to calibrate the instrument using standard gas mixture revealed that the gas sample was spread over a 3 minute peak width due to the spreading of the sample in the quartz liner in the Pyrojector. The relative IR response of CH_4 : CO_2 : CO was observed as 4 : 5: 1.

The reports on pyrolysis-FT-IR are limited. In a number of reported studies on the use of TGA-FT-IR, the volatile from the thermographic balance was allowed to pass through a gas cell while scanning FT-IR spectrum. The FT-IR signal intensity was very weak. We are able to obtain very strong signals due to the use of the light pipe in the GC-FT-IR interface instead of a gas cell. The pyrolysis products appear 2 minutes after the injection of the sample and product peaks maximized in 2.5 minutes and was spreading another 2 or 3 minutes. The reason for such tailing was the larger diameter of quartz tubing (volume = 0.5 ml) compare to the capillary column. The experiments using cryofocussing showed the elution of pyrolysis products in narrow bands comparable to capillary GC peaks. When cryofocussing was used, the products had undergone gas chromatographic separations. Both CO and methane appeared first, and CO_2 eluted later. For the comparative study of coals the spectrum collected at 2.5 minutes without the aid of cryofocussing was used as it included all the light products.

The thermal decomposition of simple organic compounds depends on the nature of functional group as well as on the pyrolytic temperature. The effect of pyrolysis temperature on acetic acid is shown in Figure 1. At temperatures below 650°C acetic acid pyrolyzed to produce small amounts of CO_2. Methane and CO were produced at 750°C and above. At 750°C tetrahydrofuran (THF, Figure 2) did not produce any oxides of carbon. However at 800°C it pyrolyzed to produce CO and hydrocarbons including methane. No CO_2 was produced from THF indicating that the oxygen from ether link can only be extracted as CO but requires higher temperatures. The amount of CO produced from THF did not increase at higher temperatures. If all the ethers behave like THF the oxygen from ethers can be extracted as CO at 800°C. Ethylacetate (Figure

3) produced CO_2 and relatively higher levels of CO compared to acetic acid. The CO production peaked at 800°C for both acetic acid and ethyl acetate and levels went down at higher temperatures. At 950°C methane and other hydrocarbons were produced the most. Methanol thermolyzed to CO, CO_2 and H_2O below 800°C and CO was the predominant species above 950°C. Ethanol produced only CO at 800°C and above.

Hydroxy benzoic acid has two functional groups -- hydroxy group and carboxylic group. Based on the results from the experiments with alcohols such as methanol and ethanol the hydroxyl group was expected to produce CO at temperatures above 800°C. Figure 4 shows that both CO_2 and H_2O were produced at lower temperatures. The oxygen in hydroxyl groups can be extracted either as water or as CO. At temperatures below 800°C only H_2O was formed. CO was formed most at 950°C.

The FT-IR spectra of volatiles from Texas lignite pyrolyzed at different temperatures is shown in Figure 5. The CO_2 and CO obtained at 700°C was from the carboxylic groups. Since the amount of CO does not increase from 700 to 800°C the ether bond represents only a small fraction of organic oxygen in lignite. The amount of CO produced at 1000°C is 50% higher than at 800°C, about 1/3 of all the CO was from hydroxyl groups. Of the oxygen extracted as oxides of carbon by pyrolysis at 1000°C, about 90% of the Oxygen was in the carboxylic groups and 10% was from the hydroxyl groups and less than 1% could be from ether groups

Premium Coal samples were also subjected to pyrolysis at temperatures from 400°C to 1000°C. Injection of packed powdered sample was easy at 700°C and above. Lower temperatures produced mostly CO2. Experiments conducted at 750°C produced CO_2, CO and CH_4 and is used for illustration. Table 1 lists all the coals and its oxygen content on an ash free basis and the products evolved. The FT-IR spectrum of the thermolysis products are shown in Figure 6. There is direct relationship between the oxygen content and CO_2 and CO produced. Higher temperatures produced slightly more oxides of carbon but did not observe any enhancement of CO.

CONCLUSIONS

Preliminary studies on Pyrolysis -GC-FT-IR of pure organic coals indicates that the analytical techniques can be developed for identifying and estimating oxygenated functional groups in organic species. The order at which functional groups thermolyzed is follows:- Carboxylic groups at 700- 800°C, ether groups at 800-900°C and hydroxy groups 900-1000°C or higher temperatures. The preliminary test results strongly supports the viability of the technique.

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Table 1 Analysis[9] and pyrolysis data of the coal samples

	Ash	Volatile	Oxygen	CO2	CO
Texas Lignite	23.6	39.5	26	0.33	0.12
Wyodak Subbitumino	6.3	32.2	18	0.15	0.05
ND Beulah-Zap	6.6	30.5	20.3	0.14	0.04
Illinois #6	14.3	36.86	13.5	0.09	0.06
Blind Canyon Seam	4.5	43.7	11.6	0.05	0.03
Pittsburgh #8	9.1	37.2	8.8	0.03	0.02
Penn Upper Free Port	13	27.1	7.5	0.02	0.04
Stockton Seam	19.4	29.4	9.8	0.02	0.01
Pocahontas #3	4.7	18.5	2.5	0.01	0.01

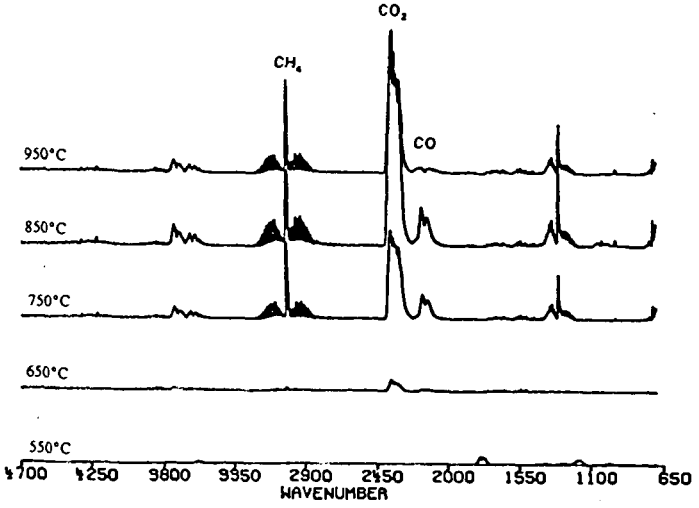

Figure 1. FT-IR spectra of decomposition products of acetic acid as a function of Pyrojector temperature.

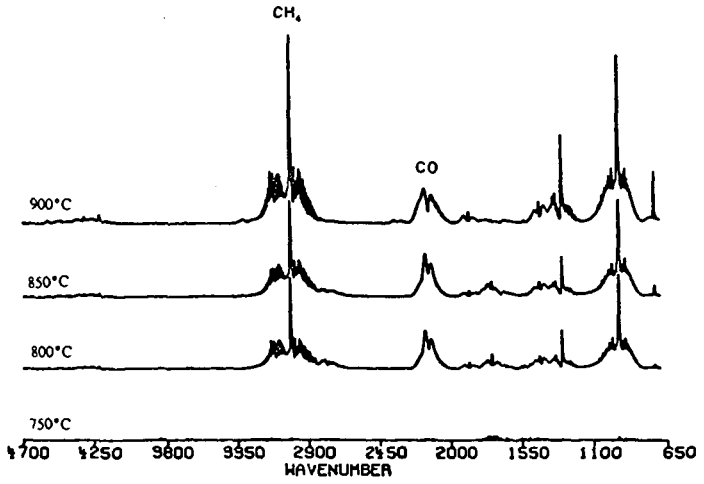

Figure 2. FT-IR spectra of decomposition products of tetrahydrofuran(THF) as a function of Pyrojector temperature.

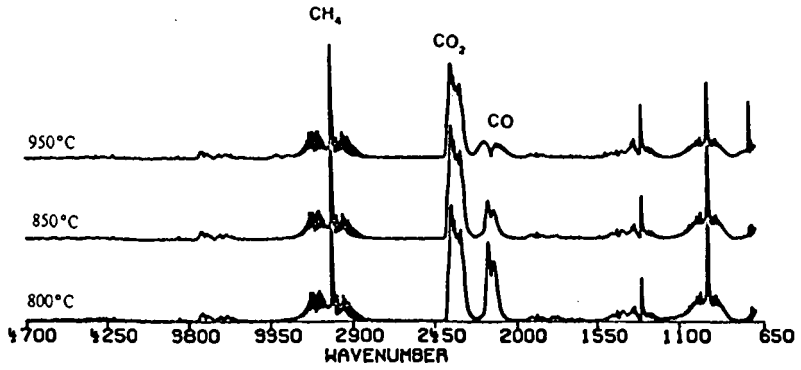

Figure 3. FT-IR spectra of decomposition products of ethyl acetate as a function of Pyrojector temperature.

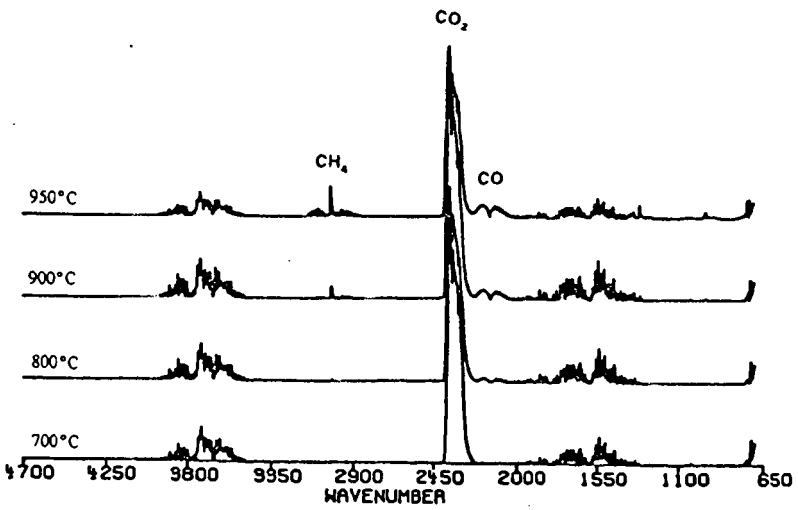

Figure 4. FT-IR spectra of decomposition products of hydroxy benzoic acid as a function of Pyrojector temperature.

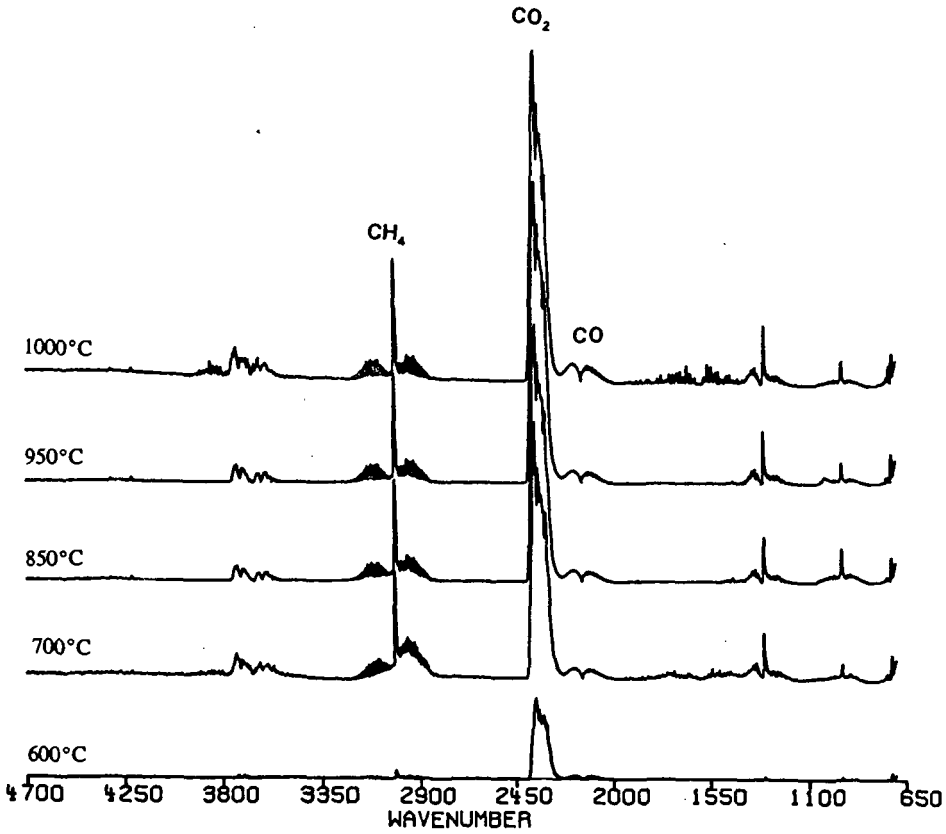

Figure 5. FT-IR spectra of decomposition products of Texas lignite as a function of Pyrojector temperature.

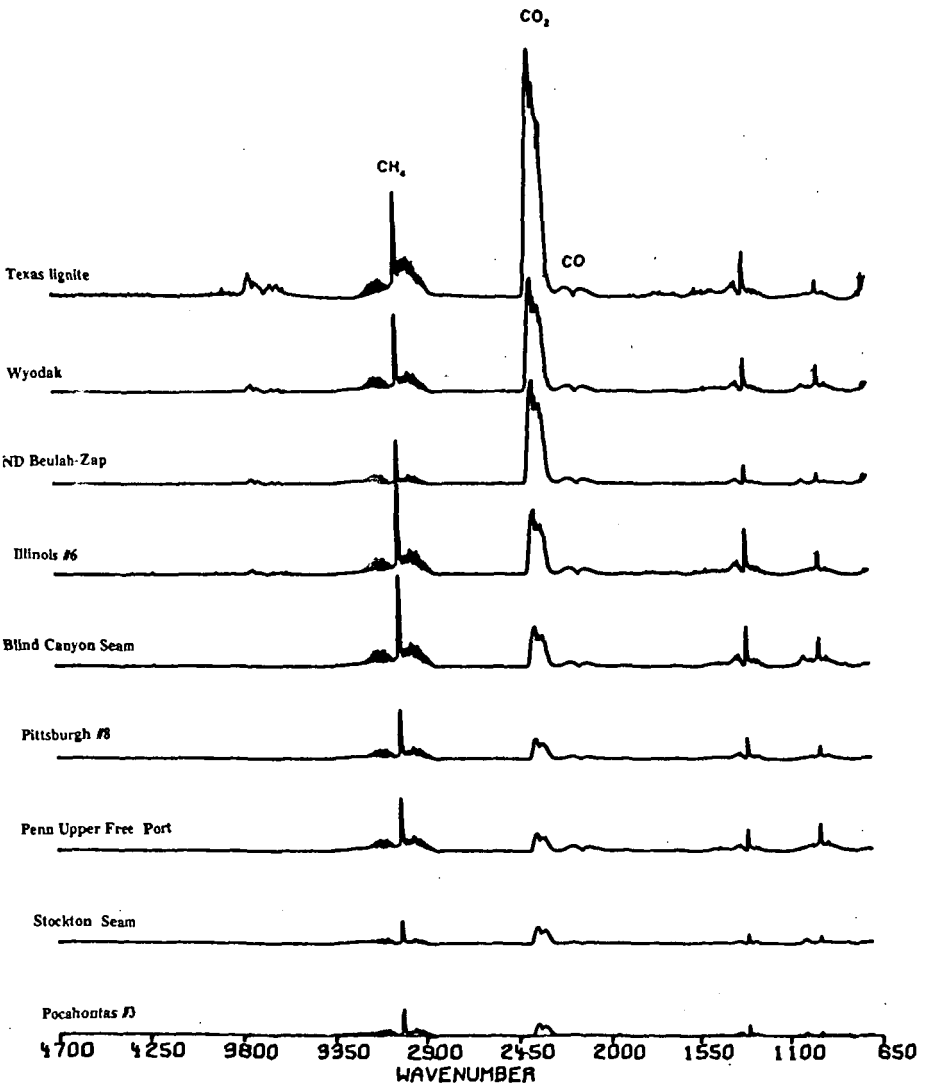

Figure 6 FT-IR spectra of pyrolysis products obtained from Texas lignite and Premium Coals. Pyrolysis temperature, 750°C